



PATENT SPECIFICATION

NO DRAWINGS

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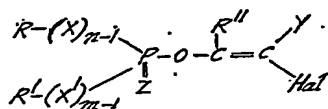
COMPLETE SPECIFICATION

Improved Pesticidal Compositions

We, CIBA LIMITED, a body corporate organised according to the laws of Switzerland, of Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The problem of prolonging the period for which pesticidal compositions containing volatile insecticidal organic phosphoric acid esters remain active is of considerable practical importance. This invention is based on the observation that the addition of a natural resin or of a chemical conversion product thereof to the volatile insecticidal phosphoric acid ester used as active principle in combating pests considerably extends the period for which the pesticides referred to remain active.

The present invention therefore provides a pesticidal composition which comprises (a) as active principle a compound of the formula



wherein m and n each represents the number 1 or 2, R and R' each represents an alkyl radical having up to 4 carbon atoms or a phenyl radical, R'' represents a hydrogen atom or a methyl group, X, X' and Z each represents oxygen or sulphur, Hal represents a halogen atom and Y represents a halogen atom or a hydrogen atom, and (b) colophony or an ester thereof, or hydrogenated colophony or an ester thereof, or an adduct of colophony with maleic or phthalic anhydride.

There may also be present, in the compositions one or more of the following additives:—silicon dioxide or a silicate, a

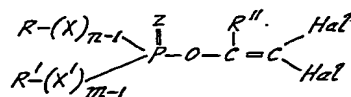
carbohydrate, or a mixture containing carbohydrates and/or proteins, which the pests can ingest. The present invention is especially concerned with a composition for combating harmful insects, for example flies or gnats and their larvae, which composition comprises

(a) dimethyl - 2,2 - dichlorovinyl phosphate, (b) colophony or an ester thereof, or hydrogenated colophony or an ester thereof, or an adduct of colophony with maleic or phthalic anhydride and (c) finely dispersed silicon dioxide or a silicate. If desired there is also present at least one of the following additives:

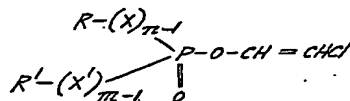
saccharose or honey, an antioxidant a (preferably red) dyestuff which attracts the insects to be combated, a bait having a smell or taste that attracts the insects to be combated, preferably a protein hydrolysate or powdered milk.

Among the compositions defined above those which contain the components (b) and (c) in a ratio of 1:1 are especially potent.

As examples of the active compounds defined above there may be mentioned those which contain the grouping

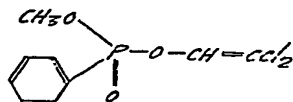


or



where n and m each represents the number 1 or 2, R and R' each represents an alkyl radical having 1 to 4 carbon atoms; R'' represents a hydrogen atom or a methyl group; X, X' and

- Z each stands for an oxygen or a sulphur atom, and Hal represents a halogen atom — for example, especially, dimethyl - 2,2 - dichlorovinyl phosphate (DDVP), diethyl - 2,2 - dichlorovinyl phosphate, di - *n* - propyl - 2,2 - dichlorovinyl phosphate, di - *iso* - propyl - 2,2 - dichlorovinyl phosphate, di - *n* - butyl - 2,2 - dichlorovinyl phosphate, di - *iso* - butyl - 2,2 - dichlorovinyl phosphate, dimethyl- and diethyl - 2,2 - dibromovinyl phosphate, methyl - ethyl - 2,2 - dichlorovinyl phosphate and the corresponding thiophosphates, more especially O : O - dimethyl- and O : O - diethyl - S - (2,2 - dichlorovinyl) - phosphate; and further the compound of the formula



- The compositions of the invention can be administered in a wide variety of forms, for example as a solid press cake (which if desired, may be moistened) or as a bait brushable on a surface; also in the form of a spray powder or an emulsifiable concentrate containing a dispersing agent or an emulsifying agent respectively, or in the form of a spray with which a coating can be produced on the object to be treated and which contains as carrier a surface-active substance; also in the form of a scattering or dusting agent containing as carrier an inert, powdered vehicle; or in the form of a solution containing the constituents (a) and (b) and an organic solvent or a mixture of organic solvents.
- In the preparation of the aforesaid spray powders and emulsifiable concentrates there may be used as dispersing or emulsifying agent, for example:
- Non-ionic products, for example condensation products of aliphatic alcohols, thioalcohols, amines or carboxylic acids with a hydrocarbon group with a long chain of 10 to 30 carbon atoms, with ethylene oxide, for example the condensation product of octadecyl alcohol with 25 to 30 mols of ethylene oxide, or of soyabean fatty acid with 30 mols of ethylene oxide, or of commercial oleylamine with 15 mols of ethylene oxide, or of dodecylmercaptan with 12 mols of ethylene oxide. Among the anionic emulsifiers suitable for use there may be mentioned: The sodium salt of dodecylbenzenesulphonic acid, the potassium or triethanol-amine salt of oleic acid or of abietic acid or of mixtures of these two acids, or the sodium salt of a petroleum-sulphonic acid.
- Suitable cationic dispersing agents are quaternary ammonium compounds, for example cetyl pyridinium bromide and dihydroxyethyl benzyl dodecyl ammonium chloride. Furthermore, there may be used mixtures of the aforesaid emulsifying and/or dispersing agents, for

example mixtures of non-ionic and anionic products.

Solid vehicles suitable for the preparation of dusting or scattering agents are talcum, kaolin, bentonite, sand, cork meal or wood meal. The various forms in which the new compositions are applied may contain the usual additions of substances that improve the adhesion, stability towards rain or the penetrating power, for example fatty acids, glue, caseins or alginates. It is also very advantageous to prepare the agents in the form of granulates.

For the manufacture of solutions for direct spraying there may be used, for example, petroleum fractions of a medium to high boiling range, for example Diesel oil or kerosene, also coal tar oils and oils of vegetable or animal origin, as well as hydrocarbons, for example alkylated naphthalenes or tetrahydronaphthalene, if desired in conjunction with xylene mixtures, cyclohexanols, ketones or chlorinated hydrocarbons, for example tetrachloroethane, trichloroethylene or trichlorobenzenes and tetrachlorobenzenes. When a hydrocarbon is used as vehicle, it is advantageous to select one that boils above 100°C.

As antioxidants, which may be present as a further constituent in the compositions of the invention, there may be used the conventional aliphatic or aromatic oxidation inhibitors, for example 1:2 - propylene glycol, 2:6 - di-tertiary butylphenol, butyl hydroxyanisole, bis - (3:5 - di - tertiary butyl - 4 - hydroxyphenyl) - methane, 3:5 - di - tertiary butyl - 4 - hydroxybenzyl alcohol, 3:5 - diisopropyl - 4 - hydroxybenzyl alcohol, or more simply constituted phenolic compounds, for example hydroquinone, resorcinol or pyrogallol.

When using the compositions of the invention as bait for ingestions by flies it is important that the mixture of the active principle and the vehicle should be of such particle size as to be easily ingested by the pest to be combated, for example by way of the proboscis of flies. Thus, for example, for combating the domestic fly, *Musca domestica*, it has been found advantageous to use an ingestion bait of a particle size of 40 μ or below.

It is possible to combat flies or gnats or larvae thereof, more especially *aedes* larvae, by using a mixture of saccharose, colophony (or an ester thereof) or hydrogenated colophony (or an ester thereof) or adducts of colophony with maleic or phthalic anhydride, dimethyl - 2,2 - di - chlorovinyl phosphate and, if desired, finely dispersed silicon dioxide and/or polyvinyl chloride, preferably by applying the mixture to water surfaces infested with the pests to be combated.

The present invention is based on the further observation that the compositions described above, more especially those which contain dimethyl - 2,2 - dichlorovinyl phosphate, and colophony or an ester thereof, and if desired

an inert vehicle that is harmless towards the organism to be treated, are surprisingly effective for combating endoparasites, more especially intestinal worms, or leeches in the liver, in warm-blooded organisms, for example in warm-blooded animals.

When used in the manner referred to above the compositions of the invention display an especially good parasitocidal action in relation to the toxicity, towards the warm-blooded animals treated, and in addition they act for a prolonged period.

The present invention also includes animal fodder and additives for animal fodder, containing a mixture of

(a) an insecticidal organic phosphorus compound of the general formulae given above, more especially DDVP, and

(b) colophony, or a derivative thereof as defined under (b) above and the additives mentioned in the previous paragraphs.

It is known that domestic animals, for example cattle, sheep, goats, horses, pigs, dogs, cats, fur-bearing animals, rabbits, fowls for example chickens, turkeys, ducks, geese and domesticated birds, more especially when young, are susceptible to infestation by endoparasites, for example intestinal worms, which cause an increased need for food and yet stunt the growth of the infested organism. In addition, an occurring infection or infestation, and

the resultant losses, reduce the average rate of growth or the yield of husbandry respectively.

By regular administration of the animal fodder or of the additives to animal fodder according to the invention the afore-mentioned disadvantages can be wholly or substantially remedied.

In general, mixed fodder containing carbohydrates, proteins, fats, minerals and, if desired, antibiotics and/or hormones, is very advantageous. Suitable fodder components are, for example, cereals, mill produce for example flour, groats or bran of rye, wheat, barley, oats, buckwheat, maize, sorghum or millet; meal of grass, clover or lucerne; molasses, meat scraps, fish meal, soya bean flour and groundnut press cake meal, cod-liver oil, lime powder, bone meal, thiamine, riboflavin, ascorbic acid or vitamin B₁₂. The compositions may also be administered in the form of a solution or dispersion in drinking water or skimmed milk, if desired admixed with a suitable dispersing agent.

The following Examples illustrate the invention, the parts and percentages being by weight:

EXAMPLE 1

Mixtures of the under-mentioned compositions were prepared for use as fly bait, and were tested to find the period for which they remained active.

Testing the period for which the baits remain active

(a) Wet baits

Mixture No. 1:	90 % of honey + 4.5% of colophony and 4.5% of finely dispersed silica + 1% of DDVP.
Mixture No. 2:	90% of honey + 4.5% of colophony and 4.5% of finely dispersed silica + 0.5% of DDVP.
Mixture No. 3:	90% of honey + 4.5% of colophony and 4.5% of finely dispersed silica + 0.1% of DDVP.
Mixture No. 4:	sugar water of 50% strength + 1% of DDVP.
Mixture No. 5:	sugar water of 50% strength + 0.1% of DDVP.

(b) Brushing baits

Mixture No. 6:	89% of castor sugar + 5% of colophony + 5% of finely dispersed silica + 1% of DDVP.
Mixture No. 7:	90% of granulated sugar + 4.9% of colophony + 4.9% of polyvinyl chloride + 0.2% of DDVP.
Mixture No. 8:	cardboard roundels dipped in a solution of 80% of granulated sugar, 5% of colophony + 5% of finely dispersed silica, 7.3% of milk powder, 1.7% of DDVP, 1% of eosine red and bitter substance (sucrose octaacetate).

Mixture No. 8 was dried at room temperature. All baits were kept in a closed thermostat at 32 to 35°C. Every month, samples of these baits were taken, admixed with 30% of water and brushed over a plate of glass and checked every 10 days for the effect on flies. For this purpose the baits were placed in Petri dishes infested with flies and covered with wire net-

ting. Evaluation was carried out after 2 hours. The results are shown in Table 1 where

+	=	within 2 hours all flies killed off
,	=	more than 50% of the flies killed off
		within 2 hours
-	=	all flies still alive
0	=	test still in progress

TABLE I

[illegible]

TABLE 1 (continued)

	Bait Mixture No.	Stored at 35°C. for	Result after days							
			200	210	220	230	240	250		
Wet bait	1	Fresh 6 months	'	'	'	'	'	'	0	
	2	Fresh 6 months	—							
	3	Fresh								
	4	Fresh 4 months								
	5	Fresh 4 months								
Brushing bait	6	Fresh 6 months	'	'	'	'	'	'	0	
	7	Fresh 6 months	'	'	'	'	'	'	0	

Remarks on Table 1

The longest active period of fresh bait was observed with Mixture No. 6 (sugar + colophony + finely dispersed silica) since after

200 days' storage it still killed off all flies and after more than 250 days still over 50%.

The order of sustained potency of the baits is as follows:

Fresh	100% days	50%
No. 6 (sugar + colophony + silica)	200	250
No. 1 (honey + colophony + silica)	140	250
No. 2 (honey + colophony + silica)	110	120
No. 7 (sugar + colophony + polyvinyl chloride)	90	250

Baits 1, 2, 6 and 7 were still active after a test period of at least 50 days, following upon 6 months' storage in the thermostat.

Bait No. 8 (cardboard roundels) likewise displayed a very good sustained action.

EXAMPLE 2

Test No. 1

Fly bait No. 8 according to Example 1, was applied to six light-green supports, each being placed in a different position in a room of about 100 m³ volume. About 1000 flies in the normal state of feeding were introduced into the room, and after 4 hours the number of flies killed within a radius not exceeding 25 cm from the bait sample concerned, was noted.

Test No. 2

6 samples of fly bait No. 8, three dry and three moistened, were placed on identical supports in the same room. About 1000 hungry

flies were introduced in the room after 4 hours the flies that had been killed were counted. Table 2 shows the result of these two tests:

Table 2—Count of dead flies after 4 hours

Test No. 1

Fly bait No. 8 (12 g in 6 positions) 28 flies (= 2.30 per g) dead.

Test No. 2

Fly bait No. 8 dry (6 g in 3 positions) 31 flies (about 5 per g) dead. Fly bait No. 8 moist (6 g in 3 positions) 62 flies (about 10 per g) dead.

EXAMPLE 3

Testing the storability of the baits

The following baits for flies, mentioned in Example 1, which after 6 months still contained DDVP, were tested for their storage life:

Mixture No. 2: Honey + [colophony + silica (1:1)] + 0.5% DDVP.

Mixture No. 6: Castor sugar + [colophony + silica (1:1)] + 1% DDVP.

Mixture No. 7: Granulated sugar + [colophony + PVC (1:1)] + 0.2% DDVP.

To establish whether the potency of the mixtures had decreased on storage, fresh mixtures were prepared by the same method, and the fresh samples and the stored samples were compared. Dilute solutions were prepared of both lots and their effect was tested by using them as ingestion baits for flies and as contact pesticides for *aedes* larvae.

Testing the stomach effect

(on *Musca domestica*)

One gram each of the fresh bait and the stored bait was diluted with 1 gram of a vehicle; for example 1 gram of bait No. 6 was mixed with 1 gram of castor sugar +

[silica + colophony (1:1)]. Thus, the initial mixture of 1% strength (10,000 parts per million) was converted into one of 0.5% strength (5,000 parts per million). Dilution was then continued at the same ratio until 2.5 parts per million was reached. The diluted mixtures prepared in this manner were pasted with 0.3 cc each of distilled water, brushed over Petri dishes and dried at room temperature. A sugar coating 2 to 3 mm thick was thus formed. Each Petri dish was infested with 10 flies and then covered with wire mesh. Evaluation was carried out after 2 hours. The results are summarized in Table 3:

TABLE 3

STOMACH ACTION: MORTALITY OF FLIES IN % AFTER 2 HOURS

Mixture No.		2		6		7	
Vehicle		Honey		Castor Sugar + Colophony + Silica		Gran. Sugar + Colophony + PVC	
Original DDVP Content		0.5%		1.0%		0.2%	
DDVP Concentration %	ppm	fresh	8 months	fresh	8 months	fresh	8 months
1	10000	—	—	100	100	—	—
0.5	5000	100	100	100	100	—	—
0.25	2500	100	100	100	100	100	100
0.12	1250	100	100	100	100	100	100
0.06	625	100	100	100	100	100	100
0.03	312	100	100	100	100	100	85
0.015	156	100	100	100	100	100	85
0.0078	78	100	100	100	80	100	25
0.0038	38	100	100	60	25	100	25
0.0020	20	100	90	50	0	60	25
0.0010	10	100	20	25	0	50	0
0.0005	5	100	0	0	0	25	0
0.00025	2.5	0	0	0	0	0	0

Testing the contact effect on *aedes* larvae
 The dilutions that had been used for testing
 the stomach effect (Table 3) were prepared
 but the only diluent used was water. 1 g of
 each preparations was mixed with 99 g of
 water and the mixtures were left untouched

for 1 day, to enable the water to dissolve the
 DDVP out of the vehicle. The further dilutions
 were then prepared. This test was carried out
 with *aedes aegypti* larvae one day old. The
 results are shown in Table 4:

TABLE 4

CONTACT EFFECT: MORTALITY OF AËDES LARVAE IN % AFTER 24 HOURS

Mixture No. Vehicle	6 Castor sugar + (colophony + silica)		7 Gran. sugar + (colophony + silica)	
Initial content of DDVP	1%		0.2%	
ppm in the water	fresh	8 months	fresh	8 months
10	100	100	—	—
5	100	100	—	—
2.5	100	100	100	100
1.2	100	100	100	100
0.6	100	100	100	100
0.3	100	100	100	100
0.15	100	100	100	50
0.075	100	0	100	30
0.038	100	0	50	20

EXAMPLE 4

(a) The following fly bait having a very prolonged action was prepared:

5 Composition:

- 80 % of fine granulated or castor sugar
 5 % of colophony
 5 % of finely dispersed silica
 7.3% of milk powder
 10 1.7% of DDVP
 1 % of eosine red powder
 0.1% of bitter principle (sucrose octa-
 acetate).

From this pulverulent mixture, a paste was
 15 prepared with 20 to 30% of water, and was

brushed over paper and over glass. This coating remained active for at least 6 months. When the bait was stored in the form of a powder, it remained active for at least 2 years.

(b) Particularly good results were obtained when the paste described under (a) above was brushed on cone sections for example of wood, since this improved way of applying the bait attracted more flies than when the mixture was applied to a plane surface.

EXAMPLE 5

Combating flies under conditions that are encountered in the case of the Mediterranean fruit fly, *Ceratitis capitata*.

20

25

Ceratitis capitata.

The following mixtures were prepared:

- (A) 5.4 g of DDVP (= 25% of total weight of the mixture)
+ 11 g of polyvinyl chloride.
+ 4.2 g of an emulsifier consisting of a mixture of (a) a condensate from 1 mol of dodecylmercaptan with 12 mols of ethylene oxide, and (b) the sodium salt of dodecyl alcohol sulphuric acid ester.
- (B) 1.0 g of DDVP (= 10% of total weight of the mixture)
+ 4.15 g of colophony
+ 4.15 g of silica
+ 0.7 g of the emulsifier described under (A) above
- (C) 0.5 g of DDVP (= 50% of total weight of the mixture)
+ 0.5 g of the emulsifier described under (A) above.

Mixture (A) and mixture (C) were prepared 1½ months, mixture (B) 7 months before application, all three mixtures being stored in a thermostat at a temperature of 35°C. The spray broths 1 to 5, shown in Table 5, were prepared from the mixtures (A) to (C). 5

TABLE 5

Spray broth No.	Mixture No. g	Protein bait (yeast hydrolysate) g	Water cc	Content of active principle in %
1	A 2	8	90	0.5
2	A 1	8	91	0.25
3	B 5	8	87	0.5
4	B 2.5	8	89.5	0.25
5	C 1	—	99	0.5

10 Petri dishes were sprayed three times with each spray broth. The dishes were then stored in a thermostat at 35°C, during which the thermostat was continuously ventilated. The first series was tested after one day's storage in the thermostat, the second series after 5 days and the third series only after 19 days storage in the thermostat. At the start of the tests, the dishes were finely bedewed with distilled water and in each dish 10 test flies (*Musca domestica*) were placed. When, after 20 hours, all flies were prostrate on their backs, the test was deemed to be positive. The dishes

were then again placed in the thermostat and on the following day once more bedewed. 10 flies were placed in each dish and the results evaluated. This was continued until action could no longer be detected. This method was used to simulate actual conditions as closely as possible, that is to say storing at 35°C, keeping the dry, climatic conditions prevailing in the Mediterranean region, with fine misting and dew formation. (In the region mentioned there is in general either no rain at all or very little rain). Table 6 shows the results obtained: 25 30

TABLE 6

ACTION OF MIXTURES IN DAYS

	Mixture No.	Period of storage prior to test					
		1 day activity in days		5 days activity in days		19 days activity in days	
		dry	bedewed	dry	bedewed	dry	bedewed
(DDVP+PVC)	1	1	1	0	0	0	0
(DDVP+PVC)	2	0	0	0	0	0	0
(DDVP+Coloph./SiO ₂)	3	2	3+	0	10	0	5
(DDVP+Coloph./SiO ₂)	4	1	3+	0	2	0	0
DDVP+Emulsifier	5	0	0	0	0	0	0
+ : not tested for a longer period.							

As can be seen from Table 6, spray broth No. 3 was most effective. The starting mixture B, from which it had been prepared, had previously been stored for 7 months at 35°C. Nevertheless, when tested after another 5 days' storing in the thermostat, spray broth No. 3 remained active for 10 days, and when tested after a further 19 days' storing in the thermostat (calculated from the time when the spray broth was prepared) it was still active for 5 days.

EXAMPLE 6

Spray powders suitable for the preparation of a spray broth for producing a coating of bait.

(a) The following mixtures were prepared:

(A) 8 parts of dimethyl - 2,2 - dichlorovinyl phosphate

8 parts of finely dispersed silica

(B) 32 parts of colophony

32 parts of finely dispersed silica

20 parts of sulphite cellulose waste liquor.

Mixture (B) was finely ground, and mixture (A) and (B) were then mixed together.

(a) The resulting mixture was stirred with a small amount of water to form a thin paste, which was then diluted with a sugar solution of 5% strength until the amount of active principle (DDVP) was 0.5%.

(b) (A) 8 parts of protein hydrolysate and 2 parts of colophony were finely ground in a ball mill.

(B) 0.5 part of DDVP and 0.5 part of the emulsifier described under (A) in Example 5 were introduced into 89.5 parts of water.

The spray broth obtained by combining constituents (A) and (B) is ready for use as a spot spray for combating *Ceratitis capitata*.

EXAMPLE 7

Emulsifiable concentrate

A mixture was prepared from

5 parts of DDVP

20 parts of colophony

10 parts of emulsifier, and

65 parts of xylene

100 parts

The emulsifier consisted of a mixture of 7 parts of the calcium salt of monolaurylbenzenesulphonic acid and 3 parts of the polyethylene-glycol ether of the monostearic acid ester of sorbitol.

The resulting product can be emulsified by pouring it into water; the spray broth thus prepared is ready for use.

EXAMPLE 8

Scattering powder

The following mixtures were prepared:

(A) 94 parts of granulated sugar

5 parts of finely comminuted colophony

(B) 0.5 part of DDVP

0.5 part of coarsely ground silica (pore diameter 100 — 150Å)

100 parts

Constituents (A) and (B) were intimately mixed. The product obtained in this manner is suitable for scattering over the surface to be treated.

EXAMPLE 9

Solution for direct spraying

(a) 1 part of DDVP

9 parts of colophony

40 parts of acetone or xylene

50 parts

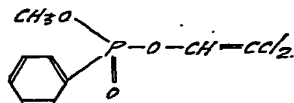
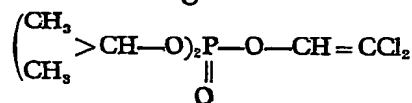
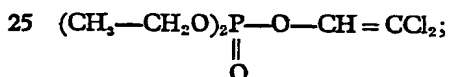
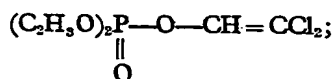
were mixed and formed a clear solution which can be sprayed over the surfaces to be treated as it is.

(b) Dusting agent

- 5 45 parts of finely comminuted colophony were incorporated in a mixture of 10 g of DDVP and 45 parts of finely dispersed silica. The resulting mixture — if desired, after admixture of an inert vehicle — can be used as
- 10 dusting agent in the usual manner.

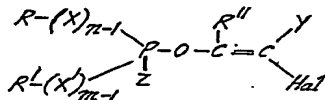
- Favourable results were also obtained when the colophony used in the mixture of Example 6 to 9 was replaced by an ester thereof, for example the pentaerythritol ester, or by hydrogenated colophony or an ester thereof, for example the glycerol ester, or by an adduct of phthalic or maleic anhydride with colophony.

- Similarly favourable results were further obtained when the DDVP used in the mixtures of Examples 6 to 9 was replaced by one of the compounds set forth above in the description, especially in the case of the following compounds:



WHAT WE CLAIM IS:—

1. A pesticidal composition which comprises
- 30 (a) as active principle a compound of the formula



- wherein m and n each represents the number 1 or 2, R and R' each represents an alkyl radical having up to 4 carbon atoms or a phenyl radical, R'' represents a hydrogen atom or the methyl group, X, X' and Z each represents oxygen or sulphur, Hal represents a halogen atom and Y represents a halogen atom or a
- 35 hydrogen atom, and (b) colophony or an ester thereof, or hydrogenated colophony or an ester thereof, or an adduct of colophony with maleic or phthalic anhydride.

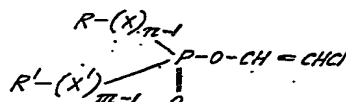
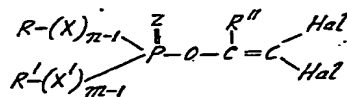
2. A composition as claimed in claim 1,

wherein there is also present one or more of the following additives:— (c) silica or silicate, (d) a carbohydrate, or a mixture containing carbohydrates and/or proteins, which is in-

50 gestible by the pests.

3. A composition as claimed in claim 2, wherein the constituents (b) and (c) are present in a ratio of 1:1.

4. A composition as claimed in any one of claims 1—3 wherein as component (a) there is
- 55 used a compound of the formula



wherein n and m each represents the number 1 or 2, R and R' each represents an alkyl radical having 1 to 4 carbon atoms, R'' represents a hydrogen atom or a methyl group and X, X' and Z each stands for an oxygen or a sulphur atom, and Hal is halogen atom.

60

5. A composition as claimed in any one of claims 1—4, wherein there is also present an inert powdered vehicle, or an organic solvent or a mixture of organic solvents as carrier.
- 65

6. A composition as claimed in any one of claims 1—5, wherein the composition is in the form of a spray powder or an emulsifiable concentrate and contains a dispersing agent or an emulsifying agent respectively.
- 70

7. A composition as claimed in any one of claims 1—5, wherein the composition is in the form of a solid cake which is, if desired, moistened, or is in the form of a bait brushable on a surface.
- 75

8. A composition as claimed in any one of claims 1—5, wherein the composition is in the form of a spray which produces a coating on the object treated and contains a surface-active agent.
- 80

9. A composition as claimed in any one of claims 1—8, wherein an antioxidant is present.
- 85

10. A composition as claimed in claim 9, wherein the antioxidant is an aliphatic or aromatic oxidation inhibitor.

11. An insecticidal composition which comprises (a) dimethyl - 2,2 - dichlorovinyl phosphate (b) colophony or an ester thereof, a hydrogenated colophony or an ester thereof, or an adduct of colophony with maleic or phthalic anhydride, and (c) finely dispersed silica.
- 90

12. An insecticidal composition as claimed in claim 11, wherein there is also present one or more of the following additives:—
- 95

- (d) saccharose or honey
(e) an antioxidant
(f) a dyestuff that is capable of attracting the organisms to be combated, or
5 (g) a bait having a smell or taste that attracts the organisms to be combated.
13. A composition as claimed in claim 1 for combating endoparasites in warm-blooded
10 dichlorovinyl phosphate and colophony or an ester thereof, and an inert carrier that is harmless towards the organism to be treated.
14. Animal fodder containing a composition as claimed in claim 1.
15. A composition according to claim 1, and 15 described in any one of the Examples herein.
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